On designing historically adequate formal reconstructions. Reply to Eric Scerri

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ON DESIGNING HISTORICALLY ADEQUATE FORMAL RECONSTRUCTIONS

REPLY TO ERIC SCERRI

Scerri's review of the first (1988) paper by Hinne Hettema and me[21] on the periodic table ended with the statement: "To conclude, I believe that the periodic table of the elements has yet to be axiomatized successfully, although the bold attempt by Hettema and Kuipers has raised a number of key issues in the philosophy of chemistry" (p. 239). The concluding section of his present review of our revised version, of 2000, begins with: "After devoting so much space to criticizing the views of Hettema and Kuipers I would like to conclude by saying that they are to be applauded for undertaking the very difficult problem of the reduction of chemistry." In view of Scerri's even more severe criticisms in the second review, its concluding statement is an even more generous statement than that of the first review. Hence, we have at least to concede that even the second version of our reconstruction and further discussion of the periodic table leaves much to be desired.

As Scerri has noticed, we did not respond in all relevant respects to his first criticisms. Apart from the fact that there was not much time between the appearance of Scerri's paper and the deadline for the revised version, it was also clear that a lot of new research would be necessary for a thorough revision. We should like to thank Scerri for his effort to clarify and elaborate a number of points in his present review. Together with the other critical points of his first review, they will certainly be of great help to somebody who might want to undertake a third attempt, in particular regarding the reduction of the periodic table.

Certainly, the main lesson to be drawn is that designing historically adequate formal reconstructions is an enormous job, not in the least "due to the difficulty of the problems it [chemistry] presents" as Scerri remarks. But it is worthwhile, for it will "deepen our knowledge of the phenomena" as he also

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[21] This reply continues in the 'we' form for it is also on behalf of Hettema, although he maintains that this reply is too apologetic.

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suggests. Moreover, we would like to add, although our reconstructions of a naïve and a refined version of the periodic table were in many historical respects problematic, conceived in purely formal terms they can still perfectly illustrate how such structuralist reconstructions may appear like and how they can be mutually related and related to other theories. That is, they may at least be conceived as toy structuralist examples with heuristic use-value. More generally, it is fortunate that Scerri's paper and some others (e.g. those of Van den Bosch and Causey in this volume and of Hamminga in the companion volume) draw attention to the structuralist approach. Unfortunately, Wolfgang Balzer, one of the pioneers of this approach, was not able to write his intended contribution on the relation between the HD-method and the structuralist approach.

For now, we should like briefly to discuss some specific points raised by Scerri, and conclude somewhat more extensively on the topic of the epistemological status of the periodic table.

Some Main Points of Full or Qualified Agreement, Sectionwise

On Section 2. It is indeed overly simplified to claim that Mendeleev designed his table with a periodicity of 8, for he was well aware of the possibility of, or even the need for different periodicities. In view of Scerri's Note 1, we are afraid that, stimulated by D. Posin's 1948 book on Mendeleev, we committed "formal romanticization," the main temptation of formal reconstruction. Moreover, despite some practical obstacles, we should have consulted Van Spronsen (1969).

On Section 3. Our presentation of the three conditions that were sufficient for the construction of the periodic table should have been amended in two respects: they were conditions as Mendeleev perceived them, with the important qualification on the notion of "similar chemical behavior" as indicated by Scerri.

On Section 4. Indeed, we did not justify our assumption that the set of chemical elements is finite. In view of our Note 2, which leaves room for elements to be discovered or artificially created, this assumption seems to become even stranger. However, as we should have mentioned, there are justifications. To understand these, one only has to investigate whether there is a certain value for the atomic number Z at which the electronic theory breaks

down in the sense that a stable electronic behavior is no longer possible.[22] There are no hard and fast rules to determine how heavy a nucleus can get before a quantum theory of its electron cloud becomes problematic. The point is most easily seen for the one electron atom, where relativistic quantum mechanics, for example, indicates that the heaviest atom theoretically possible has an atomic number of the order of 137.[23] Beyond this point, depending on the theory chosen to describe the electronic behavior, the ground state becomes unstable. For instance, according to Bohr's semi-classical method, the inner electrons of an atom with a higher number would have to travel at a speed that exceeds that of light, which is physically impossible. Similar boundaries arise in modern versions of relativistic quantum mechanics.

On Sections 4, 5 and 6. Yes, our claim that no experimental problems arose in measuring atomic mass and establishing chemical similarity is clearly overstated. From the context, however, it was also clear that we only wanted to hint at the absence of circularity problems in interpreting the relevant experiments related to the periodic table. The beryllium case shows that even this claim is false as far as Mendeleev himself is concerned for he apparently used arguments from his table. However, as Scerri also reports, in the end experiments that were independent of the table settled the valency of beryllium. Moreover, as far as we can judge from Scerri's description, the experimental problems around lutetium and lawrencium that have arisen recently are also not intrinsically related to the periodic table. To be sure, in all cases, the experiments and criticisms are certainly guided by the table, but as explained in Ch. 2 of SiS, the periodic table provides perfect illustrations of the important distinction between (intrinsically) theory-laden and (merely) theory-guided observation.

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[22] This leaves aside the discussion of the stability of the nucleus, which is a different theory and a different discussion altogether. In the context of this discussion it is conceivable, for instance, that a "stable" nucleus with a high Z value, such as 150 or more, would be stable for some time (which could be anywhere between a microsecond to a couple of seconds). While such a discovery would be highly exciting, the question of whether a stable electronic "cloud" could form around this nucleus, and whether therefore a meaningful chemistry would be possible with these heavy atoms, is yet another issue.

[23] The number of 137 is not gospel *per se*. It is, to be precise, derived from either Bohr's semiclassical theory of the atom, or the one-electron Dirac equation with a point nucleus. For instance, the Klein-Gordon equation (which does not take spin into account) has a catastrophe even when $Z > 137/2$ (see Itzykson and Zuber 1980). On the other hand, for the one electron atom, taking the physical extension of the nucleus into account pushes this point of instability to about $Z = 175$ (Itzykson and Zuber 1980, p. 83).

On Section 7. Regarding the sophisticated periodic law, it is important to make a distinction between its discovery and its status. Scerri is right in claiming that it was discovered, by Werner, independently of atomic theory. However, in view of the fact that the latter explained the former, with the consequence that table-independent measurement of the atomic number became possible, it lost its status as a proper theory in the sense of no longer having a proper theoretical term, viz. atomic number. Incidentally, we did not claim that the elaborate formalization was set up in order "to establish this trivial connection" between the naïve and the sophisticated law.

On Section 8. Scerri relativizes our distinction between a chemical and a physical conception of the atom, to some extent convincingly. However, he might have stressed our remark (reported in his Note 12) that we were sketching "the extremes of a gradual transition." Moreover, regarding *ab initio* quantum chemistry we would claim that that does not solve the Schrödinger equation atom by atom and that the relevant basis set has a very tenuous relationship with the Aufbau principle.

Let us very briefly sketch the practice of ab initio quantum chemistry to elucidate this point. In ab initio quantum chemistry the aim is to solve the electronic structure problem for either an atom or a molecule. In the most commonly practiced method, one chooses a basis set for each atom, and then proceeds to compute the overlap, potential, kinetic (1-particle) and coulomb and exchange (2-particle) integrals over the functions of the basis set. Using these integrals, a Fock matrix is constructed, which is used to iteratively solve the Fock equation until the solution is self-consistent. The point is that the wavefunction is computationally expressed as a linear combination of orbitals (a Slater determinant), which in turn are expressed as a combination of basis set functions. The electron correlation problem is generally solved on top of this Self-Consistent Field (SCF) wavefunction by either Many Body Perturbation Theory (MBPT), Configuration Interaction (CI) or more sophisticated methods such as Coupled Cluster (CC). The choice of basis set is thus pivotal to the overall quality of the calculation. If a wave function exhibits certain properties, these will only be found in the calculation if the original basis set was "rich" enough to express these properties.

The practical problem is that even a simple SCF calculation grows in complexity with the fourth power of the number of basis functions, while correlated calculations typically grow in complexity with the fifth or sixth order of the number of basis functions. The choice of a large basis set, while theoretically desirable, will therefore always present practical problems.

To sum up, we find it hard to see how Scerri's point that the Schrödinger equation is solved atom by atom can be sustained – the integrals that form the

basis of the calculation by their very definition extend over the whole molecule. If Scerri means to say that basis sets are found atom by atom then this is true in the main (though it is neither necessary nor always done). The relationship between the basis set and the Aufbau principle has also become clear: the basis set needs to furnish, at a minimum, functions of sufficient complexity for orbitals with the required properties to be created as determined by the expected results of the computational model (correlated calculations can require more extensive basis sets to deliver accurate answers than non-correlated ones; and the calculation of certain electronic properties such as dipole moments or polarizabilities requires a different creation of the basis sets yet again).

Finally, the reader who is interested in a more documented defense of the distinction between the two conceptions of the atom is referred to Hettema (2000).

On Section 9. We should have mentioned that our claimed causal correlation between "equal outer electron configuration" is an idealization; it is neither necessary nor sufficient, as Scerri documents with relevant counter examples. Fortunately, such a similar remark is not made regarding the claimed identification of the charge of the nucleus and the atomic number. As is clear from our presentation, this identity is the core of our reduction claim.

Status as Observational Law or Proper Theory

Scerri's Section 10, "Is the periodic table a true theory?", and some remarks in Section 2, give rise to a couple of remarks. Already in the first version we claimed that there had been an important transformation of the status of the periodic table: from a true theory (in the sense of a proper theory) to an observational law. Although Scerri does not agree with us that the table ever had the status of a proper theory, we are pleased to note that by stating this with such emphasis, he underwrites the existence of this distinction. The recognition of the epistemological and methodological importance of this distinction almost got lost in philosophy of science, probably due to its apparent dependence on an absolute distinction between observational and theoretical terms. In Ch. 2 of SiS it is argued extensively, in line with Nagel's original exposition, and using ideas of Hempel and Sneed, that these distinctions are independent.

In Section 2 Scerri even goes so far as to question the law-like status of the periodic table in our time in view of "the presumed reduction of this law by quantum mechanics." However, in our view, this claim merely reflects

problematic terminology. The idea is, of course, that a general observational fact loses its status as an *independent* law when it can be reduced to a theory. However, as Scerri rightly suggests, physical scientists are sometimes inclined to withdraw the law-like status altogether as soon as a law can be derived from a theory in a certain way. This is unfortunate terminology, because it suggests that reduction is a kind of elimination, whereas speaking of a "derived law," after a successful reduction, is the plausible thing to do.

In Section 10 Scerri elaborates his criticism of our claim that Mendeleev implicitly used the notion of an atomic number. Here we are inclined to disagree. Of course, by writing 'implicitly' we wanted to suggest that, although he was not using numbers, as we noted by this remark, he was using something that can be represented by numbers. To be precise, Mendeleev used a relation, chemical similarity, which was independent of atomic mass. This generated his very idea of gaps in the table based on atomic mass and the chemical similarity of known elements. The notion of a gap is a theoretical term in the sense that the existence of a gap cannot be established without using the very ideas underlying the table. And as soon as gaps are postulated, the known and unknown chemical elements can be successively numbered. To be sure, we should have made this point more explicit.

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